ThreeBond
TECHNICAL NEWS

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≪ SINX —— Basic Part ≫
Weak-UV-curing Epoxy Resin Composition

Introduction

UV-curing resin TB3000 Series have the features of excellent workability in mass production line such as one-part, 100% reaction type, and a few seconds of fast curing and excellent physical properties of the cured object.

Because acrylic oligomers are used as main component in TB3000 series, they were requested to improve their water resistance and heat resistance.

Our researchers have conducted research based on the potential of UV-curing epoxy (hereinafter referred to as "UVE") and succeeded in developing UVE series. Epoxy resins are widely used due to their excellent mechanical, electrical, and chemical properties.

UVE series have the cationic polymerization mechanism, which is different from conventional acrylic grades with the radical polymerization mechanism. As a result, the wider application has become available.

"SINX" is the development code name for "Weak-UV-curing Epoxy Resin," developed as sister grades of this UVE series.

Contents

1. About Photopolymerization Reaction Mechanism

1-1. Comparison of Radical Polymerization and Cationic Polymerization

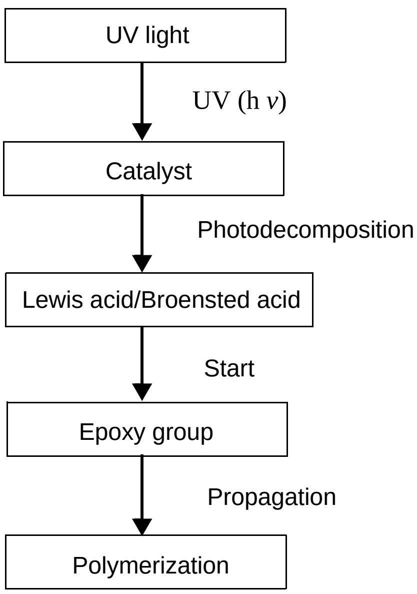
Reaction mechanism is classified roughly into the radical polymerization and the cationic polymerization type.

Table 1. Comparison of photopolymerization type

	Radical type	Cation type
Resin	Various acrylates Urethane Polyester etc.	Epoxy Vinyl ether etc.
Reaction mechanism	Free radical	Lewis acid Broensted acid
Curing speed	Fast	Medium
Oxygen blocking	Exist	Non
Curing shrinkage	Significant	Low
Adhesive property	Medium	Good
Heat resistance	Medium	Good

The radical type is composed of acrylate or unsaturated polyester/styrene. Therefore, as clearly shown in Table 1, although the curing speed is very fast, there are some problems regarding oxygen blocking, curing shrinkage, and adhesive property, etc., improvement of which are the objectives of our research.

1-2. Curing Process of Cationic UV Polymerization



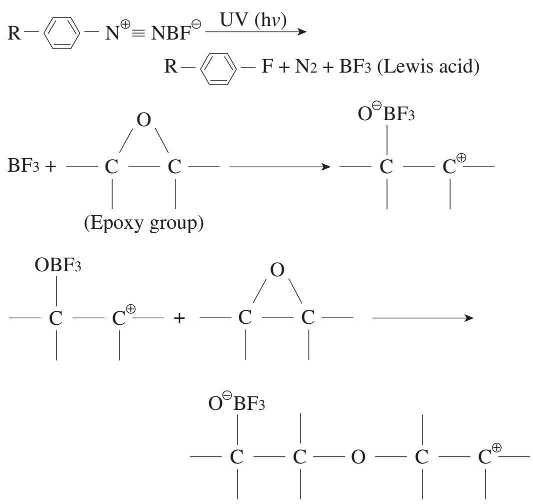
1-3. Examples of Typical Cationic Polymerization (From catalyst type)

Table 2. Typical Cationic Polymerization Initiator

No.	Type	Application
1	Diazonium salt	Coating
2	Iodonium salt	Coating Encapsulant
3	Sulphonium salt	Coating Encapsulant Adhesive
4	Metallocene compound	Screen ink Adhesive

The reaction mechanisms of the four types listed in Table 2 are shown below.

(1) Diazonium salt



(2) Iodonium salt

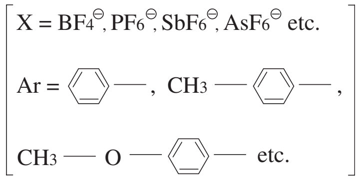
$$Ar_2I^{\oplus}X^{\ominus} \xrightarrow[\text{Solvent} - H]{UV\ (h\nu)} ArI + Ar^{\bullet} + \text{Solvent}^{\bullet} + HX\ \text{(Lewis acid)}$$

$$HX + M\ \text{(Monomer)} \longrightarrow \text{Polymer}$$

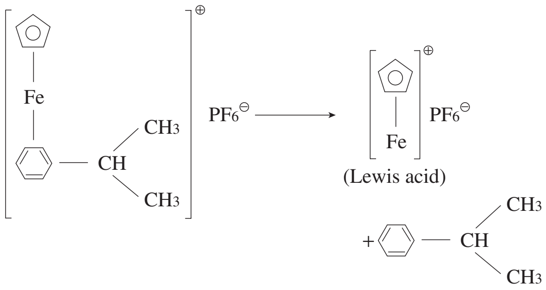
(3) Sulphonium salt

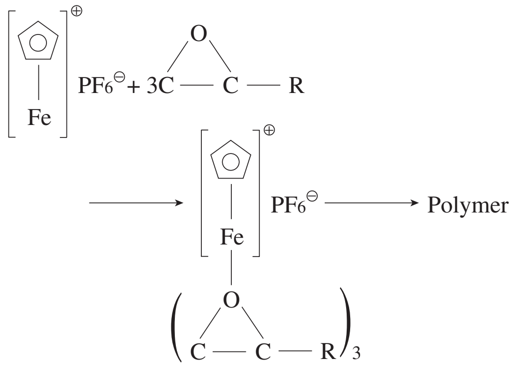
$$Ar_2S^{\oplus}X^{\ominus} \xrightarrow[\text{Solvent} - H]{UV\ (h\nu)} Ar_2S + Ar^{\bullet} + \text{Solvent}^{\bullet} + HX\ \text{(Lewis acid)}$$

$$HX + M\ \text{(Monomer)} \longrightarrow \text{Polymer}$$



(4) Metallocene compound





1-4. What is SINX?

SINX is the abbreviation of

Simultaneous Interpenetrating Polymer –
Network of Experimental Grades

This is generated from a IPN (a polymer composed of intertwined circular polymers like the rings of the Olympic Games mark).

2. Product Form

Thanks to the excellent preserving property in epoxy resin, if filler or carrier fiber is selected properly, they can obtain the following various materials.

1) Compound products (including high-load products)
2) Pre-preg products
3) Composite products

1) The high-load compounds are liquid SINX resins, with which inorganic fillers such as silica powder, silica rock, talc, and glass chop are added. They are enclosed into the desired containers according to each characteristic and applications.
   - Liquid, paste, putty, mortar, and bead
   - Plastic bottle, syringe, aluminum tube, compaq aerosol can, cartridge, role of separate paper, aluminum pouch, and AE can

2) Pre-preg
   Glass fibers impregnated with SINX resin for absorption.
   - Glass cloth, mat, tape, roving, and code shape.
   - Cover film is attached, roll magazine coiling

These pre-pregs are transformed to the requested shapes during curing. Then, FRP is obtained by UV irradiation. The molding methods include vacuum forming, posting molding, wrap around, filament winding molding, stitch method, and extrusion, etc.

3) Composite Materials
   Composite materials are combination of the SINX resin and metal plates or glass or plastic moldings. They have been developed aiming at the simultaneous development of the features of the compositions.

   Metal sheet . . . . . . Wire net, steel paper, aluminum foil, and copper foil, etc.

   Glass material . . . . Glass bead and glass plate, etc.

   Polymeric materials . . PVC tube and hard polyurethane foam, etc.

   The molding methods include compressive molding and tape lining, etc.

4) There are various technological ideas for special applications.
   (Example) 3-D printed circuit board manufacturing process
   Static UV-curing powder coating
   Bolt/nut anti-loosing cap
   Assembly of filters

3. Product Lineup

Table 3. Product lineup

Classification	Uncured object products			Cured object products	
	Form	Package/Shape	Application	Ready-made	Order-made
Compound (liquid material)	Liquid	Bottle	General purpose		
		Syringe	General purpose		
	Paste	Aluminum tube	General purpose		
		Aluminum compound	Body putty		
		333c.c. cartridge paste	Body putty		
	Cake		(1) Fixing of wires		
			(2) Solid formed		
			(3) Bolt/nut anti-loosening cap		
Pre-preg	Glass fiber	Cloth mat		(7) Vacuum formed molding	(6) Providing dent resistance to the doors of automobiles
			DIY patch		Partial curing
			Lining material		Harness fixation
		Tape	(4)(5) For piping wrapping	Composite PVC tube	(8) Assembly of filters
		Roving	For FW		
			Grip for sliding surface		(9) Honeycomb molding
Composite Material	Metal sheet	Wire net	(11) EMI		
		Steel paper	(12) EMI		
		Aluminum foil	EMI		
		Cupper foil	PC circuit board	Mat/bead pre-preg	(10) 3-D circuit board
	Glass	Bead	Light reflection		

Note: The photographs of the number (1), (2), (3),..., and (12) in the Table are shown in Photo 1, Photo 2, Photo 3,..., Photo 12, respectively.

≪ Part of application examples of the product lineup ≫

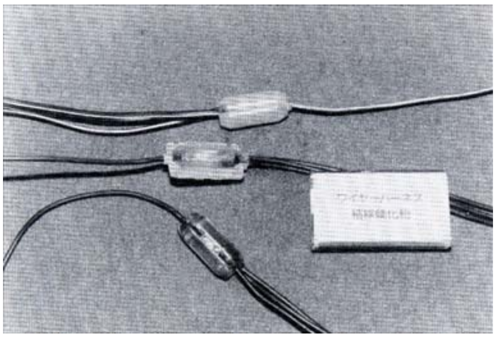


Photo 1. SINX shell pack
Wire harness connection cured objects

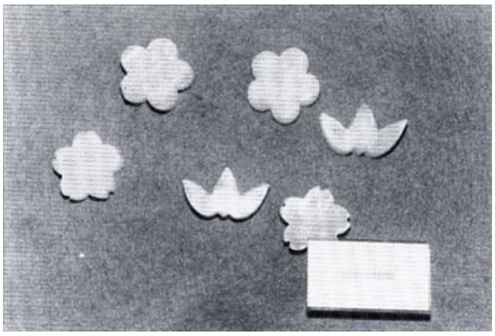


Photo 2. SINX solid resin

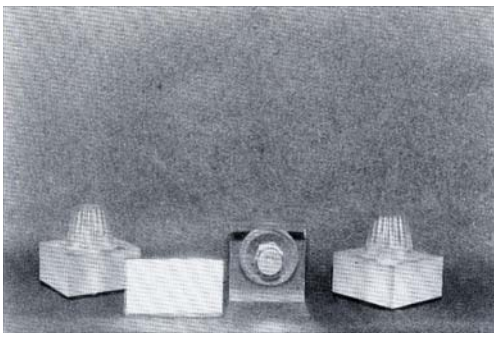


Photo 3. Bolt/nut anti-loosing caps

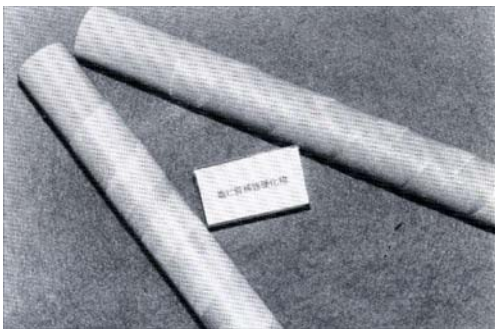


Photo 4. Polyvinyl chloride tube reinforcing cured objects using SINX pre-preg

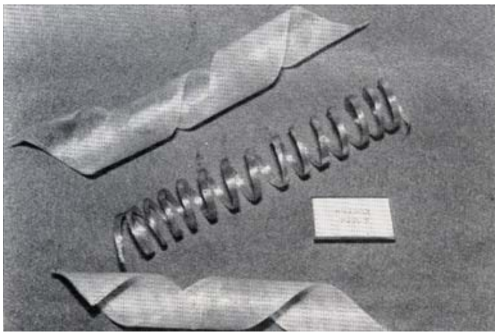


Photo 5. SINX pre-preg cured objects

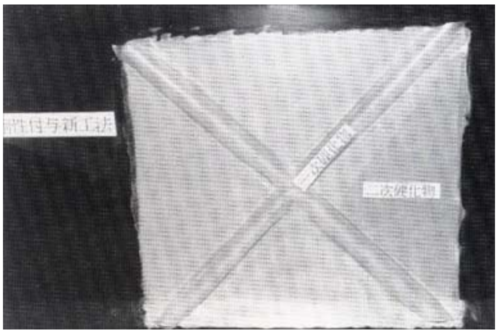


Photo 6. Providing rigidity to pre-preg (providing dent resistance to the doors of automobiles)

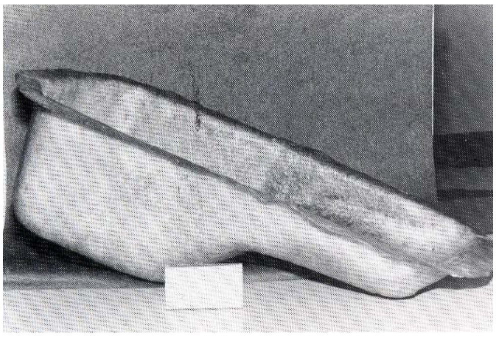


Photo 7. Vacuum forming of SINX pre-preg (oil pan)

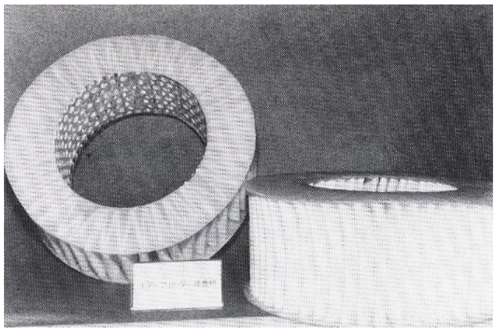


Photo 8. Air filter adhesive materials of SINX pre-preg

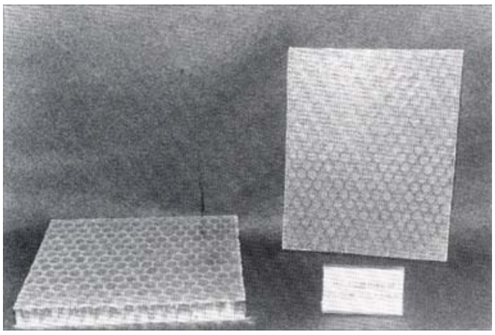


Photo 9. Honeycomb moldings using SINX pre-preg

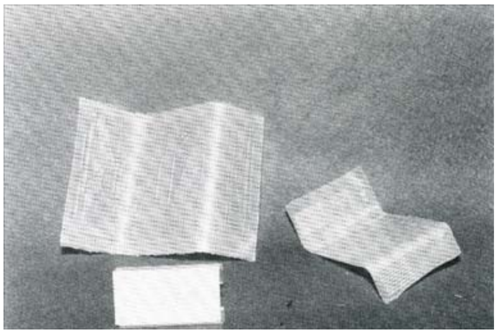


Photo 10. 3-D circuit boards using SINX pre-preg

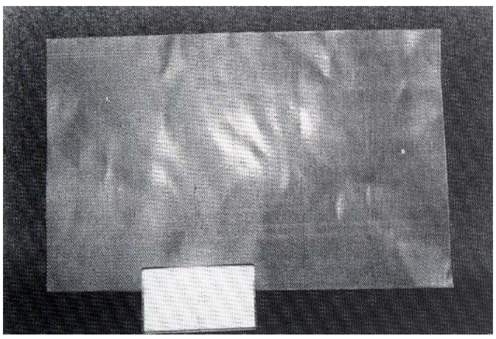


Photo 11. Bonding SINX pre-preg and copper mesh

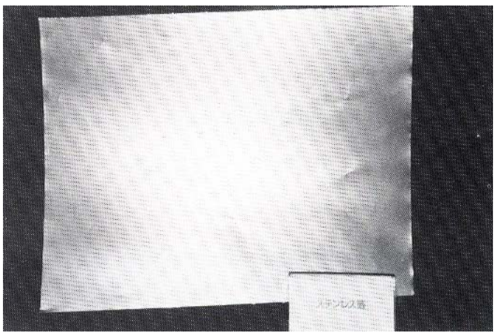


Photo 12. Bonding SINX pre-preg and stainless foil

4. Characteristics of UV-curing Type Cationic Polymerization Epoxy (SINX)

4-1. Characteristics

The characteristics of UV-curing type cationic polymerization epoxy resin are as follows:

The resins before curing have the characteristics listed below.

- One-component
- 100% reaction type
- Good preserving property
- Odor-free or light odor
- Lower toxicity

The cured objects are excellent in the characteristics listed below.

- Heat resistance
- Mechanical properties
- Electrical properties
- Chemical properties

Light-curing epoxy provided with these excellent workability and characteristics of cured objects shows the unique propagation curing property in addition. This is the property that once the (cationic) polymerization reaction starts, curing continues to be completed without external energy supply.

4-2. Curing by Sunlight (Weak UV)

After assembling the equipment below, put liquid SINX in it to the depth of 1mm. Take the equipment to the outside and check the curing time of SINX.

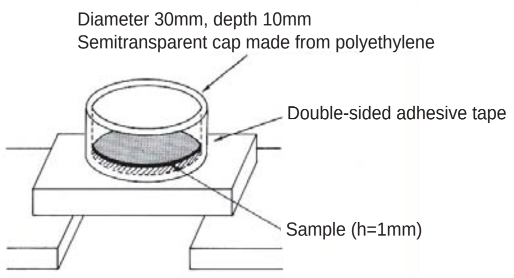


Figure 1. Curing equipment by sunlight (weak UV)

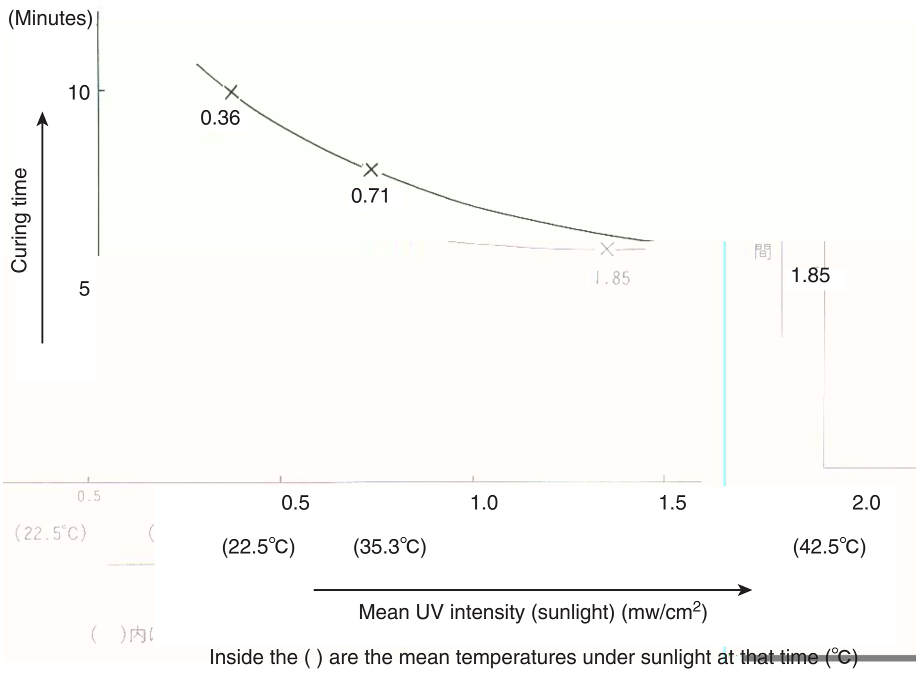


Figure 2. Curing time by sunlight (weak UV)

4-3. Depth Curing Property

After assembling the equipment below, fill the sleeve made from Teflon with liquid SINX. And then, perform a given UV irradiation from above the Teflon sleeve and measure the thickness of the cured part of liquid SINX.

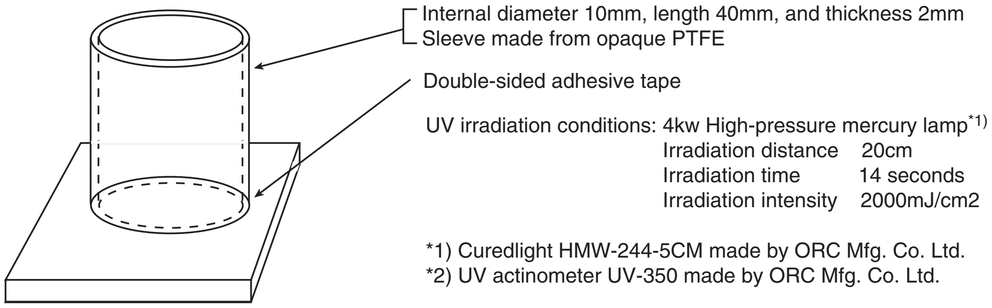
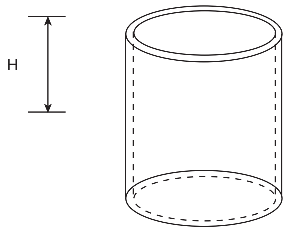


Figure 3. Depth curing property measuring equipment

Table 4. Exposure time and depth curing property after completing irradiation

T: Time	H: Curing depth
10	4.8mm
1	5.2mm
4	5.4mm
8	6.5mm
24	8.7mm



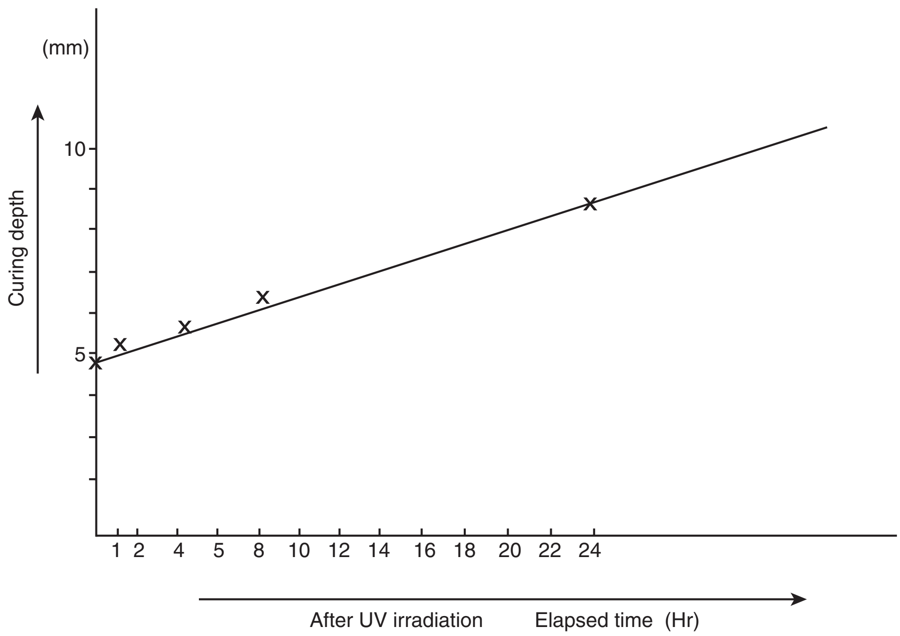


Figure 4. Exposure time and depth curing property after completing irradiation

As shown in Table 4 and Figure 4, depth curing proceeds with elapsed time.

4-4. About Characteristics of SINX Compound (shell pack)

1) Properties and performance values

(1) Properties and performance

Table 5

Appearance	Transparent Non-fluid cake	
Specific gravity	1.14	
Standard curing condition	10 seconds	Irradiator . . . . 4kw Focused cold mirror Illumination . . . . 142mw/cm^2 Irradiation distance 15cm
Hardness (Shore D)	25°C . . . . 88 50°C . . . . 78 80°C . . . . 72 100°C 42	

(2) Preserving property

Preserve at cool and dark place.

Avoid exposure to direct sunlight or weak UV (260nm), especially.

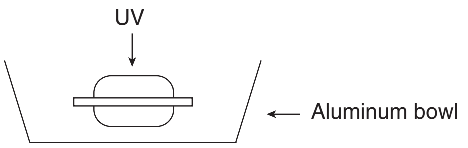
2) Curing property

(1) Objectives

Samples should be cured after they are UV-irradiated within 10 seconds or less.

(2) Irradiation method

After setting the shell pack together to put into an aluminum cup, deliver to the beltline, then irradiate from the above.



(3) Irradiator

Compare type	4000CM (ThreeBond Automation Equipment Co., Ltd.)
Output	4 kw
Lamp	Focused cold mirror

(4) Irradiation conditions

Irradiation distance	15cm
Irradiation time	5 seconds, 10 seconds, and 15 seconds
Illumination	142mw/cm^2

(5) Decision

Measurement of curing

Measure the hardness of the cross sections by cutting the UV irradiated samples after each designated time.

Hardness tester D Type (ASTM-D-2240)

(6) Result

Table 6 (D Scale)

Irradiation time / Elapsed time	5 seconds	10 seconds	15 seconds
After 12 hours	64 to 70 Low part is not cured	76 to 82 Completely cured	80 to 84 Completely cured
After 24 hours	68 to 74 Low part is not cured	80 to 86 Completely cured	80 to 86 Completely cured

(7) Conclusion

Since the measured hardness of the samples of 10 seconds and 15 seconds irradiation are ranged 82 to 86 after 3 days, the sample of irradiation curing of 10 seconds has passed with the above-mentioned conditions.

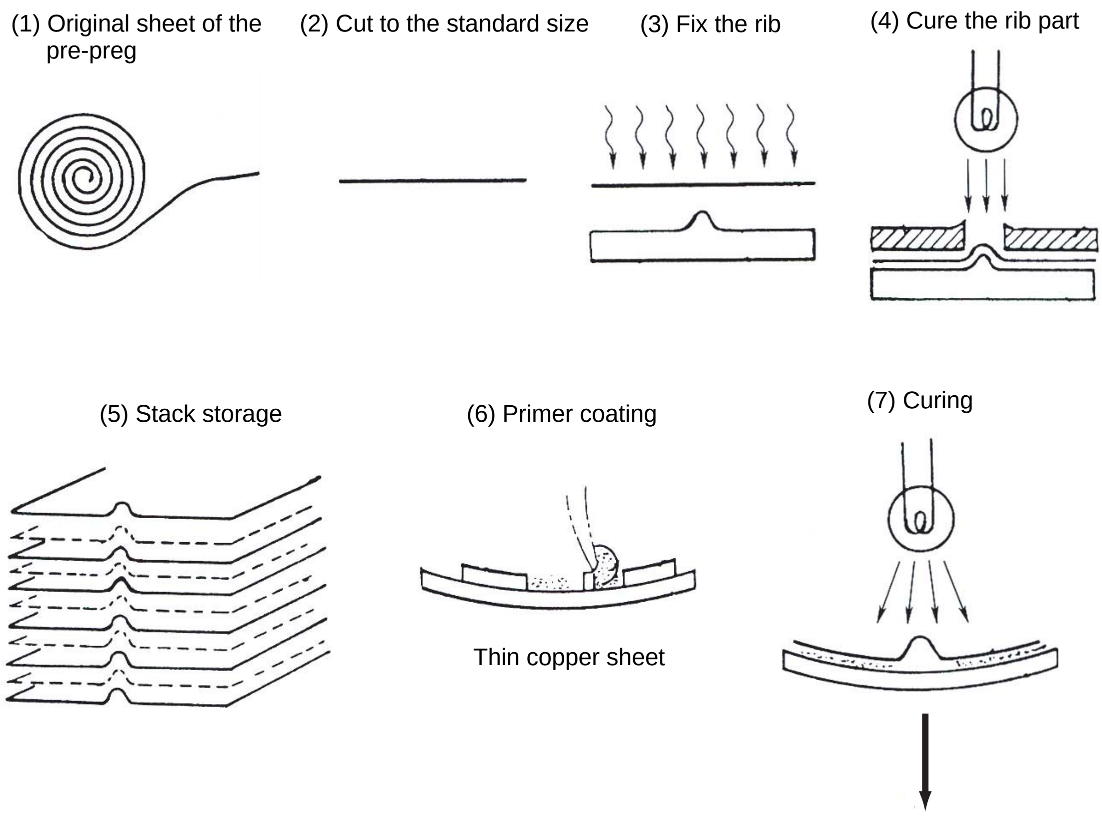
3) Hardness

(1) Temperature - hardness

After exposing the samples, which were cured under the standard curing condition, for 24 hours, expose the cured objects at each temperature for 60 minutes for stabilization, then measure the hardness immediately.

Table 7

Temperature	Hardness (Shore D)
50°C	74 to 78
80°C	66 to 72
100°C	40 to 42



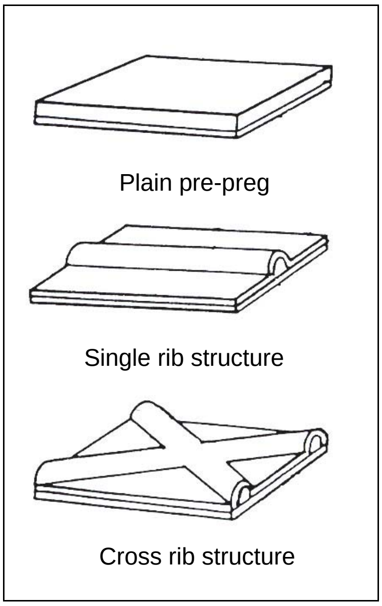


Figure 5. The method to provide rigidity to thin steel sheet by SINX re-preg

Table 8

Sample	Thickness (mm)	Weight (g)	Bending rigidity ($kg•mm^2$)
Single steel sheet	0.3	19	4,000
+ Plain pre-preg	1.3	22	20,400
+ Single rib	1.3	23	75,900
+ Cross rib	1.3	24	93,000
Single steel sheet	0.38	24	8,100

- Chopped strand mat pre-preg 1.0mm
- $40mW/cm^2$ × 30 seconds, from ribR3
- Cold-rolled steel sheet, JIS (Japanese Industrial Standard) G3141, 150 × 50 × 0.3mmt

(1) Original sheet of the pre-preg

Dip the glass cloth into SINX undiluted solution to impregnate. And then, stick the separate paper on it and store it in dark place.

(2) Cut to the standard size

Before using, take the original sheet of the pre-preg from the storage area and cut to the standard size.

(3) Fix the rib

Place the pre-preg, which was cut to the standard size, on the master block, flow hot air by a dryer to adjust shape.

(4) Cure the rib part (primary cured object)

Mask all the surface except the rib part. And then, irradiate UV to cure the rib part.

(5) Stack storage

Store the pre-pregs made in the step (4).

(6) Primer coating

Coat SINX primer on the thin steel sheet, and affix the pre-preg to the rib made in the step (4) together.

(7) Curing (secondary cured object)

Irradiate UV to the whole to bond and cure the pre-preg.

As shown in the Table 8, SINX pre-preg values of bending rigidity are about 5 to 20 times higher, compared with thin steel sheet. Of course, the values may depend on the shape of the rib.

As these mentioned above, SINX pre-preg indicates a future direction in providing dent resistance (rigidity) while weight saving trend has progressed in various market.

5. Future Prospects and Objectives of UV-curing Type Cationic Polymerization Epoxy Resin

There are generally two-component type and one-component type epoxy resin adhesives. The two-component type is supplied with the epoxy resin and curing agent in liquid or paste. The two component are mixed to form adhesion layer and cured at room temperature or heat cured. The one-component type is supplied as the mixture with potential curing agent in paste, therefore users can use it immediately without mix work.

SINX belongs to the type containing potential curing agent in a broader sense. To achieve higher performance after the cationic catalyst curing system is measured in its own reactivity, it will be the key to research for new types of epoxy resin or system availability.

Conclusion

SINX is the newly developed product. Only part of the features has been introduced in this issue. We think that it has great future potential.

We also wish to present the application part of SINX in the near future.

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